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MORPHOLINE PROPERTIES: A LITERATURE REVIEW

Report No 89-131-K

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ABSTRACT

General properties of morpholine, its liquid/vapour distribution, ionization, and thermal decomposition properties are reviewed, with discussions of station experience and the work program. Morpholine ionization increases with an increase in temperature to about 100°C and decreases at higher temperatures. The pH of a morpholine solution decreases as temperature increases. The distribution coefficient for morpholine is less than 1 below 170°C and greater than 1 above 170°C. The thermal decomposition half-life of morpholine varies from 30 days at 260°C to 30 seconds at 560°C and follows first order kinetics. Confirmed thermal decomposition products are given. There has been little work to characterize the dependence of morpholine breakdown on pH, oxygen concentration, surface area, and metal composition although these have all been mentioned as possible influences.

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EXECUTIVE SUMMARY

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This survey was conducted as part of the COG-funded program, work package 1906, "Evaluating Amines for Secondary Side Water Treatment".

The purpose of the survey was to determine the background in morpholine properties which are relevant to the secondary side water treatment in nuclear power plants. General properties, liquid/vapour distribution, ionization, and decomposition properties are reviewed, with discussions of station experience and the work program.

Ionization properties appear to have been well researched although there is only one set of complete experimental data up to 300°C. Ionization constants for morpholine have been determined experimentally and calculated using thermodynamic data. The value of the constant in the literature varies. Morpholine ionization increases with temperature to about 100°C above which it decreases with temperature. However, the change in the dissociation constant of water, K_w, with temperature in combination with morpholine ionization properties results in a decrease in pH over the range 0 to 300°C. The pH decreases with temperature from 9.24 at 25°C to 6.1 at 300°C for a 10 mg/L morpholine solution.

Relative volatility was measured by 5 authors and distribution by one. Calculated values were given by one author and these values disagreed somewhat with the experimental values. Experiments showed that the distribution coefficient for morpholine is less than 1 below 170°C and tends to increase with temperature to a limiting value of about 1.35 above 230°C although there is some discrepancy between authors.

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The thermal decomposition half-life of morpholine is 30 days at 260°C, 3.8 days at 300°C, 24 hours at 345°C and 30 seconds at 560°C. The reaction appears to follow first order kinetics. Confirmed decomposition products are given.

Almost all of the experimental work discussed was performed with pure morpholine solutions, and, apparently, zero oxygen concentration although this was assumed rather than measured. There has been little work to characterize the dependence of morpholine breakdown on pH, oxygen concentration, surface area, and metal composition although these have all been mentioned as possible influences. This data is required to understand where in the system morpholine is likely to decompose and how fast in order to better understand the effectiveness of morpholine station chemistry and its effects on corrosion.

The work in our partially COG-funded feedwater chemistry program will attempt to address these issues.

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To Mr. B. Collingwood
Manager, CANDU Owners Group
Design and Development-Generation

MORPHOLINE PROPERTIES: A LITERATURE REVIEW

1.0 INTRODUCTION

This survey was conducted as part of the COG-funded program, work package 1906, "Evaluating Amines for Secondary Side Water Treatment".

The purpose of the survey was to determine the background in morpholine properties which are relevant to the secondary side water treatment in nuclear power plants. General properties, liquid/vapour distribution, ionization, and decomposition properties are reviewed, with discussions of station experience and the work program.

The following data bases were surveyed :

STN International Chemical Abstracts
Electric Power Research Institute (EPRI)
Department of Energy (DOE)
Update of DOE data base

Information from some internal reports from Ontario Hydro and other companies and recent conferences is also included.

1.1 Current Use of Morpholine in Nuclear Power Plants

As of 1980/1/, 80 % of Canadian nuclear plants used morpholine. In the USA, 4 % of nuclear plants used morpholine. In 1986, the use of morpholine was unchanged in Canada, but had doubled to 8% in the USA/2/, still very much below the use in Canada. The interest in morpholine has increased primarily because it has proven useful in alleviating erosion-corrosion problems. France uses morpholine in its PWRs to combat erosion-corrosion/3/. Morpholine is also used in some nuclear plants in Britain, Spain, Belgium,Germany, India, Pakistan and Switzerland/2/. Much EPRI-funded work focusses on using morpholine in conjunction with boric acid. Current EPRI contracts relating to morpholine are

discussed elsewhere/43/. There is now considerable interest in the oxygen scavenging properties of morpholine/5/.

1.2 Desirable Amine Properties for Nuclear Power Plant Water Treatment

For an additive to be useful for neutralizing free acids and maintaining a basic pH, the following characteristics must be considered:

- Ionization constant
- Distribution ratio or partition coefficient between aqueous and vapour phases.
- Thermal stability under steam-water circuit conditions

The ionization constant of a compound should be one which yields high basicity at all system temperatures since maintaining an appropriate alkaline pH minimizes ferrous alloy corrosion.

If the distribution ratio was unity at all temperatures the liquid and vapour phase concentrations would be the same throughout the system at any temperature. However, higher concentrations in crevices and in the steam generator liquid phase than in the steam may be desirable for corrosion resistance. In that case, a distribution ratio less than one would be desirable.

Thermal stability is important in maintaining system chemical concentrations and minimizing the concentration of decomposition products which may enhance corrosion at worst, or render the chemical treatment less effective at best. These decomposition products may also influence cation conductivity levels which are used to indicate levels of anionic impurities.

2.0 MORPHOLINE PROPERTIES

2.1 General

Cyclic ether amine, or tetrahydro 1,4 - oxazine, commonly called morpholine because of a supposed identity with the basic ring of morphine, was discovered by Knorr in 1889./6/ It became commercially available in 1935/7/.

Morpholine is a water-white liquid with an ammoniacal odour. It can be manufactured by cyclization of diethanolamine with sulfuric acid or by cyclization of B,B'-dichloroethylether with ammonia/8/. Morpholine is commonly prepared by reacting diethylene glycol with ammonia/9/.

Table 1 shows physical properties of morpholine./7/

TABLE 1

PHYSICAL PROPERTIES OF MORPHOLINE

Molecular Weight	87.12
Freezing Point °C	-4.9
Boiling Point °C, 760 mm Hg	128.9
Flash Point °C, (open cup)	37.8
Density, g/cc 20 °C	0.994
Conductivity mho/cm x 10^{10}	6

Morpholine is reported to be completely miscible in water; it does not form an azeotrope with water/7/.

Morpholine is reputed to react with carbon dioxide as follows/10/:

$$OC_4H_8NH + H_2O + CO_2 \rightarrow OC_4H_9N.H_2CO_3 \quad (1)$$

This carbamate supposedly sublimes without decomposition on heating at 95 - 100°C/6/. According to Riddle (1986)/9/, in plants equipped with a deaerating heater, the stripping action of the steam decomposes the amine-carbamate and removes some of the carbon dioxide. This property enables morpholine to be regenerated by venting a deaerating heater./9/ It is not clear whether this has been substantiated experimentally.

2.2 Ionization

Morpholine ionizes as follows:

$$C_4H_9NO + H_2O \leftrightarrow C_4H_9NOH^+ + OH^- \quad (2)$$

The base ionization constant K_b is:

$$K_b = \frac{[C_4H_9NOH^+][OH^-]}{[C_4H_9NO]} \quad (3)$$

$$pK_b = -\log K_b \quad (4)$$

Ionization constants for morpholine have been determined experimentally and calculated using thermodynamic data. The value of the constant in the literature shows some variation.

Table 2 summarizes the findings in the literature of pK_b at different temperatures:

TABLE 2

IONIZATION CONSTANT OF MORPHOLINE AT DIFFERENT TEMPERATURES

T	pK_b						pK_w	pH(10 mg/L) (morpholine)
°C	a /11/	b /11/	c /12/	c /13/	c /13/	c /14/	/15/	/11/
0	5.831	5.832	5.837					10.03
20				5.70	5.50			
25	5.500	5.500	5.505	5.61	5.67	5.508	14	9.24
50	5.315	5.315	5.309					8.60
75			5.208					
100	5.197	5.202	5.178					7.64
125			5.204					
150	5.291	5.301	5.278					6.98
160							11.55	
175			5.394					
180							11.41	
200	5.543	5.560	5.549				11.30	6.52
225			5.740					
230							11.21	
250	5.940	5.964	5.965				11.20	6.23
275			6.222				11.22	
300	6.478	6.509	6.512				11.30	6.10

a. Calculated using $\Delta Cp^{25},a$ = 43.01 J/mol K for acid ionization of the morpholinium ion.

b. Calculated using average $\Delta Cp,a$ = 46.44 J/mol K (0-300°C) for acid ionization of the morpholinium ion.

c. Experimental Values

Data prior to 1965 showed the ionization constant only for room temperature/13/. There are discrepancies between the constants.

In 1966, Hetzer et al/14/ found that the pK_a was 8.492 using temperature variations data. They used silver-silver chloride and Pt-H_2 electrodes and measured EMF. They found that the dissociation constant (K_a) for the process

$$MH^+ + H_2O <-> M + H3O^+ \quad (5)$$

could be represented by the following equation:

$$-\log K_a = 1663.29/T + 4.1724 - 0.0042239T. \quad (6)$$

They also found that at 25°C, $-\log K_a$ is 8.492 (pK_b = 5.508), H_o is 39030 joules $mole^{-1}$ S_o is -31.7 joules deg^{-1} $mole^{-1}$, and Cp_o is 48 joules deg^{-1} $mole^{-1}$ where H_o, S_o, Cp_o are the enthalpy and entropy of formation and Cp_o is the heat capacity./14/

Christensen et al showed that the H_o and S_o values for proton dissociation from the primary and secondary aliphatic protonated amines increase in a regular, additive manner as methyl groups are substituted on the hydrocarbon chain./16/

Mesmer and Hitch found the variation of K_b with temperature experimentally in 1977/12/.

Cobble and Turner calculated pK_b at different temperatures in 1985/11/.

From the above data, it can be seen that morpholine is a stronger base as temperature increases to about 100°C after which the amount of ionization decreases with temperature. However, the change in K_w with temperature in combination with morpholine ionization properties results in a decrease in pH over the range 0 to 300°C.

2.3 Liquid/Vapour Distribution

There was not a great deal of consistency in the definition of distribution ratio or partition coefficient particularly in earlier works. Distribution ratio, distribution coefficient and partition coefficient appear to be used interchangeably although, strictly speaking, the partition coefficient applies to the partitioning between liquid phases. In this review, the definition used in the recent works of Balakrishnan, Turner, and Lewis is used. The distribution ratio is defined as:

$$K_d = \frac{\text{molality base in vapour}}{\text{molality un-ionized base in liquid}} \quad (7)$$

This quantity is independent of pH. The distribution coefficient may be considered to be independent of concentration at low concentrations of solute although, over the entire mole fraction range, it does depend on concentration/17/.

However, just as the distribution coefficient will vary with temperature at constant pressure, it will vary with pressure at constant temperature although the dependence on pressure tends to be very small/44/.

Distribution data may also be represented by the Henry's Law Coefficient, K_h, where:

$$K_h = P/x_b \quad \text{(ideal gas)} \tag{9}$$

$$K_h = f_b/x_b \quad \text{(non-ideal gas)} \tag{10}$$

where P = total pressure

f_b = fugacity of the gas of component b

x_b = molality of b in liquid phase

The distribution coefficient is related to the Henry's Law coefficient by:

$$K_d = K_h \, Z/P \tag{11}$$ /42/

where Z = compressibility factor (e.g. of steam)

The distribution coefficient tends to be more pressure dependent than the Henry's Law Coefficient as shown below:

$$\left(\frac{\partial \ln K_d}{\partial P} \right)_T = \left(\frac{\partial \ln K_h}{\partial P} \right)_T + \left(\frac{\partial \ln Z}{\partial P} \right)_T + \frac{1}{P} \tag{12}$$

$$\left(\frac{\partial \ln K_h}{\partial P} \right)_T = \frac{V_b}{RT} \tag{13}$$ /44/

where V_b = partial molar volume (e.g. of amine)

The pressure dependence tends to be very small./44/

Many of the older reports and reports on station experience defined the distribution ratio as:

$$K'_d = \frac{\text{molality base in vapour}}{\text{molality base in liquid}} \tag{14}$$

This is actually the relative volatility and depends on pH.

The reason for pH dependence of the relative volatility was first described by Przybylinski in 1979./18/ The pH dependence of the

relative volatility value was explained to be the previously unrecognized cause of many discrepancies between reported "distribution ratio" values. This pH dependence arises because the amine is only volatile in the form of its molecular species (A). At low and intermediate pH, a significant fraction of the amine is present as a cationic species (AH^+). Under these conditions, the amine's volatility is reduced below its maximum value i.e.

$$\text{Relative Volatility} \leq \text{Distribution Ratio} \qquad (15)$$

The distribution ratio or partition coefficient is related to the relative volatility by:

$$K_d = RV/(1-@) \qquad (16)$$

where K_d = distribution coefficient
RV = relative volatility
$@$ = degree of dissociation = $[BH^+]/([BH^+] + [B])$

For example, a morpholine solution at a pH of 9 (4.5 mg/L) and room temperature will have a RV that is 82% of the K_d. However, a 10 mg/L morpholine solution at 250°C will have a RV that is 99.7% of the K_d.

Liquid/vapour distribution coefficients were measured experimentally using a variety of methods. Experimental apparati for measuring relative volatility ranged from batch distillation to static tests to flow-through/recirculation loops.

Table 3 summarizes all relative volatility and distribution data found in the literature. Discussions of this data are found in sections 2.3.1 and 2.3.2.

2.3.1 Relative Volatility

Albrecht et al (1976) measured relative volatility at atmospheric pressure in an all-glass distillation apparatus./19/ Morpholine analysis was done by refractive index, thus the use of very high morpholine concentrations.

Cuisia (1977) found that the average morpholine relative volatility at atmospheric pressure was 0.48. He used a once-through boiler with a test duration of 6 hours. The temperature appeared to be between room temperature and 100°C although a specific temperature was not given in the paper. Amines were analyzed by direct titration with HCl and methyl purple indicator./20/

TABLE 3

RELATIVE VOLATILITY AND DISTRIBUTION COEFFICIENTS AT DIFFERENT TEMPERATURES

T °C	Conc. mg/l	Relative Volatility	ref.	Distribution Coefficient	ref.
0	10	0.079	11d	0.089	11c
				0.089	11d
25	10	0.204	11d	0.240	11c
				0.240	11d
				0.240	11
50	10	0.407	11d	0.513	11c
				0.513	11d
100	10	1.023	11d	1.380	11c
100	10*	0.4	22	1.288	11d
100	25	0.48	20	0.457	11
100**	1000	0.46	1		
100	60000	0.3	19		
100	70000	0.4	19		
100	140000	0.6	19		
100	770000	0.73	19		
100	970000	0.88	19		
150	10	1.622	11d	2.400	11c
				1.995	11d
				0.759	11
156	25	0.48	1		
158	20	0.72	1		
158	21	0.72	21	0.83	21
158	186	0.86	21	0.9	21
160	448	0.88	21	0.9	21
170	10*	0.98	22		
180	179	1.00	21	1.04	21
180	436	0.98	21	1.01	21
182	25	0.98	21	1.10	21
198	10*	1.6	22		
200	10	1.862	11d	3.02	11c
200	199	1.12	21	1.16	21
200	436	1.01	21	1.03	21
				2.188	11d
203	21	1.11	21	1.23	21
216	10*	1.4	22		
230	414	1.31	21	1.33	21
231	10*	1.2	22		
237	20	1.30	21	1.41	21
244	10*	1.2	22		
250	10	1.698	11d	2.951	11c
				1.862	11d
				1.288	11
251	20	1.22	21	1.30	21
254	10*	1.3	22		
255	185	1.33	21	1.36	21
263	10*	1.2	22		
273	331	1.30	21	1.32	21
279	10*	1.3	22		
285	22	1.32	21	1.38	21
292	10*	1.3	22		
300	10	1.230	11d	2.344	11c
300	10*	1.3	1	1.288	11d
300	409	1.33	21	1.34	21
304	10*	1.3	22		
312	10*	1.2	22		

* concentration not mentioned in paper. Value inferred from pH of case studies

** temperature not given. Value inferred from pressure

c. Calculated using $\Delta C_{p,h}$, 25°C = 138.8 J/mol K.

d. Calculated using average $\Delta C_{p,h}$ = 167.7 J/mol K (0-300°C)

Balakrishnan (1978) used natural recirculation and static modes of operation to determine relative volatilities./21/ He found that the relative volatility decreased as the temperature increased in the range 175 to 300°C, but increased as the concentration increased. He deduced that a distribution ratio greater than one was possible if a morpholine/water azeotrope existed above 175°C although this contradicts an earlier reference./7/

Przybylinski (1979) used a glass distillation flask./18/ He calculated relative volatility by the derived formula

$$RV = \log[(A_1-A_v)/A_1]/\log[(L-V)/L]. \quad (17)$$

where RV = relative volatility
A_1 = Initial weight of amine in the solution
A_v = Total weight of amine boiled off
L = Initial weight of amine solution
V = Total weight of vapour boiled off

The formula is completely accurate for a single plate distillation assuming only that RV is constant during the distillation. This assumption is essentially true as long as the concentration of the amine in the boiler is always below 10 g/kg so that there is no molecular interaction, and the pH and temperature are constant. The solution may be buffered to achieve constant pH./18/

Anerousis et al (1979) performed a flowing experiment lasting 4 days in total in a stainless steel research boiler and reported pressure versus relative volatility data. No change was found in relative volatility with amine concentrations. However, no concentration ranges were given and several amines were tested simultaneously./22/

Conn and Von Nieda gathered a list of morpholine relative volatility and equilibrium properties in a literature survey conducted in 1980/1/.

2.3.2 Distribution Coefficient

Cobble and Turner (1985) produced calculations of distribution coefficients for morpholine at different temperatures. They also calculated the solution properties for a 10 mg/L solution of morpholine/11/.

Lewis et al (1985) produced a graph of Henry's Law coefficient, K_h (atm) vs. Temperature/23/. The Henry's Law coefficient is less pressure dependent than the partition coefficient and data

from the literature appeared to conform better than a plot of K_d vs temperature to the following relationship:

$$\log K_h = -4270/T + 32.42 - 8.259 \log T \qquad (18)$$

The effect of hydrolysis of metal-ion impurities and their complexing with the added base was examined and thought to be negligible at the metal concentrations likely to be present in the type of boilers to which amines would be added./23/

The distribution coefficient of morpholine tends to increase as temperature increases. Experimental measurements show that the distribution ratio is below 1 up to a temperature of about 170°C and increases to a limiting value of about 1.35 to 1.4 although there is some discrepancy between authors.

Discrepancies between calculations based solely on thermodynamics and actual measurements may imply non-ideal behaviour such as molecular interaction in solution or improper measurements.

2.4 Thermal Decomposition

Dow Chemical first reported morpholine to be stable up to 288°C. Above this temperature, they reported that it decomposes and forms ammonia, although decomposition is not significant until 649°C./24/

Samuel/25/ (1955) carried out thermal decomposition tests in an autoclave. Morpholine decomposition reached 40 % in 48 hrs for a solution of 1.74 g/L at 308°C. Breakdown products were presumed to be ethanolamine, diethanolamine, and some primary amines. Amino-alcohols could result from opening of the C-O bonds of the ring molecule. None of these compounds was confirmed by analysis.

Other tests (1955)/26/ on the decomposition of morpholine indicated that about half would decompose at 538°C and at (apparently) atmospheric pressure.

Jacklin (1955)/27/ used a flow-through system, an experimental high-pressure boiler with a super-heater. All tests were run with 100 % make-up of feedwater. Feedwater morpholine concentration was 34 mg/L. The test was allowed to run for several hours until equilibrium was reached before any readings were taken. Morpholine breakdown was determined by analyzing for ammonia. This is valid only if all the nitrogen in the decomposed morpholine ended up as ammonia. The results obtained are shown in Table 4.

TABLE 4

MORPHOLINE BREAKDOWN
(calculated using data from reference/27/)

Temperature °C	Pressure psi	(MPa)	pH average	pH calculated from NH_3 concentrations	Percent Breakdown calculated from NH_3 concentrations
242	500	(3.5)	8.3	8.5	2.3
270	800	(5.5)	8.5	8.9	1.6
313	1500	(10.3)	8.0	9.2	3.2
354	2500	(17.2)	8.3	9.3	4.9

The relatively low pH found in the steam condensate was initially attributed to unusually high absorption of carbon dioxide by the stored feedwater. However, since the feedwater alkalinity was 10 mg/L, the CO_2 content of the condensate was not more than 3 or 4 mg/L. Instead of being 34 mg/L, the morpholine content of the steam must therefore have been very low to explain the low pH measured in the condensate. If so, the percentage breakdown of morpholine must have been very high under all of the conditions reported/27/.

Agarwala (1982) stated that morpholine decomposed by 2 to 5% in boilers at pressures of 95 kg/cm^2 (9.3 MPa) and 108 kg/cm^2 (10.6 MPa). All tests were carried out with 100% make up of feed water in service boilers of a steam generation plant. Saturated steam temperature was 306°C./28/ No boiler volume was given so residence time is unknown and thus an estimate of decomposition rate cannot be made.

Dauvois et al (1986) studied morpholine decomposition both in the plant and in the laboratory/29/. They found that regardless of the composition of the solution, there was no specific action of pure morpholine on cation conductivity. The amine is fully exchanged and does not contain acids.

They subjected solutions of dilute morpholine to a temperature of 300°C under an inert gas blanket for 4 to 21 days, in order to identify acidic ions. After cooling down the autoclave, the solution was drained under inert atmosphere, into a tinted glass, since light exposure and oxygen were found to change the composition of thermolyzed morpholine solutions at room temperature. The presence of weak acids was indicated./29/

The pH of the remaining basic solution was higher than the pH of the initial fresh solution proving the presence of bases stronger than morpholine, coming from morpholine thermal decomposition. /29/

A figure in the report showed the evolution of some decomposition products i.e. acetic and formic acids, of 0.01 M morpholine solution, at 300°C, versus time./29/ No attempt was made to define an order of reaction. From this and other data they proposed some morpholine decomposition mechanisms. Intermediate breakdown products included diethanolamine, ethanolamine,glycol, ammonia, and acetic and formic acids.

Monoethanolamine, diethanolamine, and some simple primary amines may also be formed./9/

Feron et al./30/ studied the thermal stability of morpholine in a static autoclave and a recirculation loop which simulated the PWR secondary circuit. They concluded that the thermal decomposition of morpholine begins with hydrolysis into other amines and glycol. Then, in the presence of oxygen, metallic catalysts and high temperature, aldehydes and organic acids are formed. Acetate and formate were the main decomposition products observed in laboratory and loop tests. They concluded that copper and carbon steel surfaces were not an important factor in morpholine decomposition, but that oxygen level has a major effect on morpholine stability in PWR secondary circuits.

Lewis et al (1988)/31/ studied the thermal decomposition of morpholine at temperatures from 250°C to 560°C at pressures from 500 to 2100 psig in a small flow-through system which passed through an oven or fluidized-bed furnace. They found a half-life of 30 seconds and first order kinetics for thermal breakdown at 560°C. The half-life of morpholine at 345°C was approximately 24 hours. Decomposition during a 50 second exposure time at 320 to 370°C was negligible. At 250°C in water, no decomposition of morpholine occurred in three days. However, its disappearance was considerably accelerated in the presence of oxygen. The reaction of morpholine decomposition appeared to be surface dependent in an all-metallic test loop. Low-molecular-weight carboxylic acids were among the decomposition products; largest quantities appeared during

transient periods of rapid breakdown.

Gilbert et al (1989)/32/ studied the thermal decomposition of morpholine in a static autoclave at temperatures up to 300°C. Half-lives of morpholine were found to be 30 days, 9.2 days, and 3.8 days at temperatures of 260, 280, and 300°C respectively. The reaction kinetics were found to be first order with decomposition rate constants of 2.67, 8.73 and 21.25 x $10^{-7}s^{-1}$ at 260, 280, and 300°C respectively. The activation energy, E_a, was found to be 131.9 kJ/mol. Ammonia, ethanolamine, 2-(2-aminoethoxy) ethanol, methylamine, ethylamine, ethylene glycol, and acetic and glycolic acids were identified as the major breakdown products. All tests were performed in a 316 SS, 300 mL autoclave. The ratio of the metal surface area to solution volume was 270 cm^2/180 mL at room temperature and the surface was polished prior to testing. Initial solution concentration of morpholine was 150 mg/L for all tests. A mechanism was proposed in which oxygen was involved in the formation of acetic and glycolic acids. The proposed decomposition route was validated in the field by tracking these breakdown products in water samples taken from the Gentilly 2 power plant.

Morpholine may have promise of being an oxygen scavenger since oxygen appears to be involved in the breakdown of morpholine. The presence of oxygen appears to promote a stoichiometric degradation of morpholine/5/.

Toelgyessy et al (1986) studied the effect of gamma radiation on an aqueous solution of morpholine on the basis of UV spectrum measurement, chemical oxygen demand, short-term oxygen demand determination, and Petter's kinetic test of biodegradation. They found that the biodegradability of the model solution became substantially worse after irradiation. No indication of the radiation flux was given./33/

3.0 STATION EXPERIENCE

Morpholine has been used successfully in boilers operating at 1600 psi and 537°C./7/

Morpholine has been compared with other amines as early as 1956 when Ristroph and Yorkgitis compared morpholine and cyclohexylamine in power plants. They wanted to minimize pickup of iron and copper by controlling pH in the steam-feedwater cycle of a high-pressure, reheated, controlled-circulation boiler./34/

France and Britain have switched to morpholine from ammonia primarily to avoid erosion-corrosion problems./4/ This impact is

attributed primarily to the increase in liquid film pH in two-phase regions as a result of the lower steam/liquid distribution coefficient of morpholine compared to ammonia./36/

At the Vandellos power plant in Spain, the incorporation of morpholine as a substitute for NH_3 was found to temporarily decrease the course of erosion-corrosion, but afterwards increased it./35/ No clear reason for this was given and the station subsequently changed to AMP.

3.1 U.S. Experience

Use of morpholine as a pH control additive at Prairie Island and Beaver Valley significantly reduced iron levels in the condensate and feedwater./36/

Decomposition of morpholine leads to formation of formic and acetic acids which increase blowdown cation conductivity. However, the observed increase is less than 0.2 μS/cm, and the sensitivity of cation conductivity to strong acid anions does not decrease significantly./36/

Tests at Beaver Valley which runs only on morpholine showed an unknown compound which was suggested to be diethanolamine but this was not confirmed. Make-up water was a significant source of organic acids and mass balance studies should be considered in future studies. It was recommended that these studies should include decomposition compounds of morpholine and corrosion products./37/

Riddle et al, in their 1986 survey of PWR experience with morpholine reported that the only negative feature associated with the use of morpholine is a slightly elevated cation conductivity level, presumably from organic acids formed from decomposition of morpholine. However, current experience at Beaver Valley and Palisades showed that industry-accepted AVT guidelines for cation conductivity limits for the steam generator blowdown can be implemented (e.g., cation conductivities less than 0.8 μS/cm can usually be maintained in these two plants)./2/ However, current EPRI guidelines allow the cation conductivity to be "corrected" to compensate for acetate and formate./39/

Riddle et al also noted that morpholine levels were not generally characterized in the plants responding to the survey. They recommended that plants contemplating the use of morpholine should set up adequately designed monitoring programs to enable the behaviour of morpholine, its possible decomposition products, and the effect of morpholine on secondary cycle chemistry parameters and corrosion products to be fully

evaluated. Only Beaver Valley and Palisades performed steam cycle morpholine measurements on a routine basis. One reason that morpholine analyses have not been performed more often is that the most commonly used analytical procedure requires carbon disulfide, a toxic and highly flammable solvent. The procedure used by Beaver Valley does not use carbon disulfide but uses the colorimetric reaction of morpholine with the sodium salt of 1,2-naphthoquinone-4-sulfonic acid which is good for 0 to 6 mg/L ± 0.3mg/L./2/

Morpholine was used at TMI-1 during June to August in 1988 in an attempt to reduce boiler differential pressure/38/. It was added at 4 to 8 mg/L. The effects were assessed using corrosion product transport studies. Morpholine reduced corrosion product transport as measured by dissolved and suspended iron by a factor of 2 to 3. Up to 200 µg/L formate and 50 µg/L acetate were found. The highest concentrations were found in the MS Drains./42/

The EPRI PWR Secondary Water Guidelines endorse morpholine as an alternative to ammonia for secondary water chemistry pH control but it is stated only that morpholine concentration be used as a diagnostic parameter. However, the advantages which are responsible for the adoption of morpholine chemistry are lost if the morpholine level falls below a critical level. This critical level appears to be plant specific and so could not be given in general guidelines.

Studies are required to determine the optimum levels of morpholine needed to minimize sludge loading of our steam generators./39/ The optimum morpholine concentration thus appears to be plant specific and should be determined by plants based on corrosion product transport surveys.

3.2 Canadian Experience

Ontario Hydro sampled for organics at Nanticoke and Lakeview thermal power stations which were operating on morpholine feedwater treatment at the time. It was found that 10% of base-neutral organics was ethyl morpholine. Formic and acetic acids ranged from 9 to 200 µg/L./40/

Gilbert and Saheb measured the average relative volatility for morpholine in steam-water cycle of Gentilly-2. They found relative volatilities of 1.15, 0.91, 1.07, at the steam generator, high-pressure side of the turbine, and low-pressure side of the turbine respectively. Comparison with data reported in the literature revealed that measurements with systems in thermodynamic equilibrium for a given temperature tended to overestimate the volatility of morpholine compared to the HP and LP sides of the turbine. Therefore the system was not at equilibrium. They confirmed the presence of two decomposition products of morpholine; methylamine and ethylamine./41/

4.0 DISCUSSION WITH RESPECT TO THE WORK PROGRAM

The literature surveyed yielded information for dissociation constants, vapour/liquid distribution, and thermal decomposition of morpholine.

Dissociation properties appear to have been well researched although there is only one set of complete experimental data up to 300°C. Relative volatility was measured by five authors and distribution by one. Calculated values were given by one author and these values disagreed somewhat with the experimental values. There is some recent data on thermal decomposition products of morpholine.

Almost all of the experimental work discussed was performed with pure morpholine solutions, and, apparently, zero oxygen concentration although this was assumed rather than measured. There has been little work to characterize the dependence of morpholine breakdown on pH, oxygen concentration, surface area, and metal composition although these have all been mentioned as possible influences. This data is required to understand where in the system morpholine is likely to decompose and how fast in order to better understand the effectiveness of morpholine station chemistry and its effects on corrosion.

The work in our partially COG funded feedwater chemistry program will attempt to address these issues.

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